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FABRICATION OF CELLULOSE-BASED CHITOSAN COATING ADSORBENTS FOR CAPTURE TO CADMIUM (II) AND ZINC (II)

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ABSTRACT

Cellulose fiberous adsorbent (CCCF) was prepared from sugacane agasse by coating chitosan on the fiber surface. The chitosan layer coated on the cellulose fiber enhanced adsorption to Cd^{2+} and $Zinc^{2+}$. High efficency of the CCCF of removal % for the Cd (II) and Zn (II) was with 93.7 % and 93.0 %, respectively and the adsorption capacity was 2.0 mg/g.

Keywords: cellulose, chitosan, heavy metal ions, fibrous adsorber, adsorption.

1. INTRODUCTION

Cellulose ($(C_6H_{10}O_5)_n$) is the most abundant organic polymer in nature and polysaccharide consisting of linear chain of several hundred to many thousands of β(1→4) linked D-glucose units. Therefore, there were many reports on uses of cellulose in the chemical modification to cellulose derivatives. For example, consisted of the OH group is easy to chemically modify. The resulting decrease in water absorption capacity leads to an increase in the durability and stability of the cellulose. Thus, such treatment steps was conducted in order to increase the chemical activity and physical strength of the product [1]. On the other hand, chitosan is secondary abundant polymer often seen as a white powder and has interesting properties of biocompatibility, biodegradability and non-toxicity. Among them, it was used well-known that complex associations with metal ion through specific interactions was found for the amino groups ($-NH_2$) [2]. But chitosan is water soluble polymer, although the complex formation is effective, meaning much difficulty in separation of the metal-chitosan complex from water phase. As based on this ability for biopolymer chitosan, the greatest potential has been seen for biomass application in the treatment of heavy metal-contaminated water [3, 4]. with the solidified modification. Using chitosan to coating on cellulose has advantages in increase of the physical and chemical ability of cellulose, which is easily obtained from natural plant source [5, 6].

In the present paper, biomass source of sugarcane bagasse was used for cellulose and the cellulosic OH group was partially oxidized. Then, chitosan coating was taken on the fiber surface for fibrous adsorbent. The main purpose of this research is the elimination of heavy metals Cd^{2+} and Zn^{2+} in aqueous solution medium [7, 8] by using chitosan-coated-cellulose.

2. MATERIALS AND METHODS

2.1. Chemicals and equipment

Chitosan was purchased from Spectrum Chemical & Laboratory Products Co., Ltd (China), cellulose was purified from sugarcane bagasse sourced from Ben Tre Province, Vietnam. Chemicals used in the analytic processes such as NaOH, NaOCl, H_2SO_4 and KIO_4 were obtained from Merck (Germany). Aqueous heavy metal ions Cd^{2+} and Zn^{2+} were prepared at each 10 ppm from concentrated extract.

2.2. Chemical treatments of sugarcane bagasse and modification to chitosan coating on cellulose

The treatment steps are depicted in Fig. 1. First step consisted of a deep cleaning and the elimination of contaminants from the material. The bagasse was well washed with water and dried under sunlight, then immersed in water at 80 °C and finally the water was replaced every 5 hours [9, 10]. The cleaned bagasse was then dried in the sample drier for 24 hours at 60 °C and used for acid and alkali treatments and bleaching to cellulose fiber (CF).

Washing sugarcane bagasse (10 g)
↓ Acid treatment with 300 mL of 4 % H_2SO_4
Stirring (80 °C, 1.5 hour)
↓
Water washing and filtration with MiliQ
↓ Alkali treatment with 300 mL of 10 %
Stirring (80 °C, 12 h)
↓
Water washing and filtration with MiliQ
↓
Stirring (50 °C, 3 h)
↓ Bleaching with 100 mL of 10 % NaOCl
Immersion in MiliQ at room temperature for 24 h
↓
Cellulose Fiber (CF)

Figure 1. Chemical treatment processes of sugaecane bagasse for cellulose fiber.

Oxidized cellulose (ODCF) was obtained by an oxidation process using potassium periodate (KIO_4) as shown in Fig. 2 [10]. The oxidation process was followed with immersion of

3 g of CF in 400 ml of MiliQ containing 0.04 M oxidizer with reaction for 3 hours at 60 °C. The treated fiber was washed again with MiliQ and dried at 60 °C. Chitosan-coated-cellulose (CCCF) was obtained through the following process: immersion of 3 g of the ODCF in a mixture of 400 ml acid acetic 2 % and 8 g of chitosan for 2 hours. The fibers were then washed with MiliQ and dried at 60 °C for 24 hours. Following this process, the CCCF was tested for Cd (II) and Zn (II) adsorption.

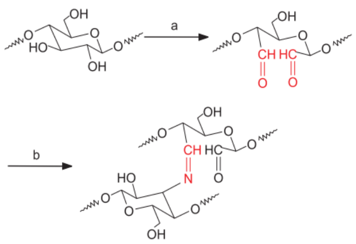

Figure 2. Scheme of oxidation using KIO_4(a) and chitosan coating (b) onto cellulose.

2.3. Heavy metal adsorption by chitosan coating cellulose fiber

Batch adsorption experiment to Cd^{2+} and Zn^{2+} was carried out at different pH in aqueous solution. The pHs used in the experiments were ranged from 2 to 10 and adjusting with 0.1 M NaOH or 0.1 M H_2SO_4. The amount of the CCCF used was 0.5 g with 50 ml of aqueous solution and the ion concentration of Cd^{2+} and Zn^{2+} was 10 ppm. The sample was shaken for 120 minutes at 150 rpm at room temperature.

3. RESULTS AND DISCUSSION

3.1. Fabrication of chitosan coating cellulose fiber

As seen in Fig. 3, the pictures of CF, ODCF and CCCF had different colors, meaning that the white color changed to white yellow color after CF was treated with KIO_4. Then much deeply yellow color was obtained in the CCCF, when chitosan was coated on the ODCF.

CF CDCF CCCF

Figure 3. Pictures of CF, ODCF and CCCF.

3.2. Characterization of the chitosan coating cellulose fiber

As viewed from the SEM pictures in Fig. 4, the surface structure of the CF had noticeable changes after the acid and base treatments, oxidation and chitosan coating. It was seen that the surface of the ODCF exhibited more aggregation of the cellulosic fibers and less smooth surface.

However, after the oxidation process of KIO_4 was done, the smooth surface was observed in the CCCF and significant durable surface was obtained as compared to the ODCF. Results of FT-IR analysis are shown in Figure 5 for the three fibers. The transmittance spectra had broaden peak at 3344 cm^{-1}indicating the appearance of the hydroxyl (-O-H) group of the cellulose. At 2894 cm^{-1}, the appearance was for $-CH_2$ streaching and at 1640 $cm^{-1}$for water peak. The spectroscopy of the ODCF and CCCF exhibited weaken transmittance band at 1750 cm^{-1}, indicating appearance of new C=O bond formed by the KIO_4 oxidation process. After chitosan treatment a decline was seen at the 1550 cm^{-1} for the appearance of the N-H group. Also, the appearance of the N-H group can be used as evidence on the chitosan coating through the covalent bond C=N.

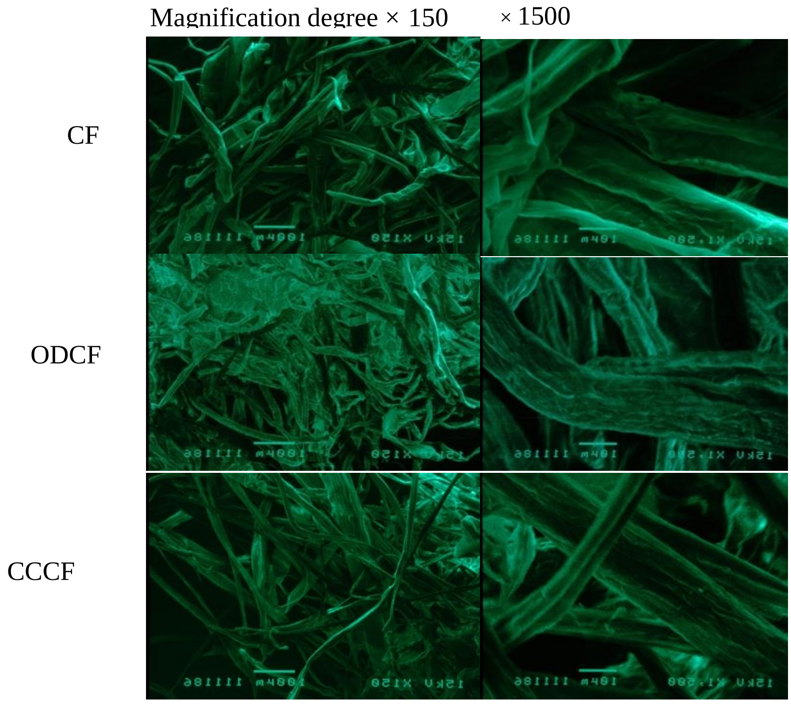

Figure 4. SEM pictures of CF, ODCF and CCCF at 150 (left) and 1500 magnification (right).

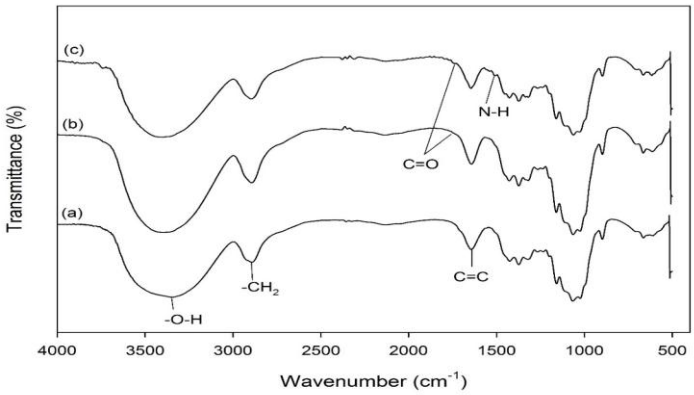

Figure 5. FT-IR spectra of (a) CF (b) ODCF and (c) CCCF.

3.3. Adsorption properties of chitosan-coated cellulose fiber

For Cd (II) and Zn (II) removal % is plotted with pHand is shown in Fig. 6. When pH was over 8, the white precipitation turbisity of the solution was observed. When pH increased, the heavy metal ions were precipitated as $Cd(OH)_2$ and $Zn(OH)_2$[11]..The results showed that the removal rate dependedon the pH by colloid formation at alkali region. The higher removal Cd (II) and Zn (II) was found in the CCCF,meaning that the complex formation of chitosan to each ion was effective. At over pH8, the colloid precipition might enhance the removal of the Cd(II) and Zn(II).

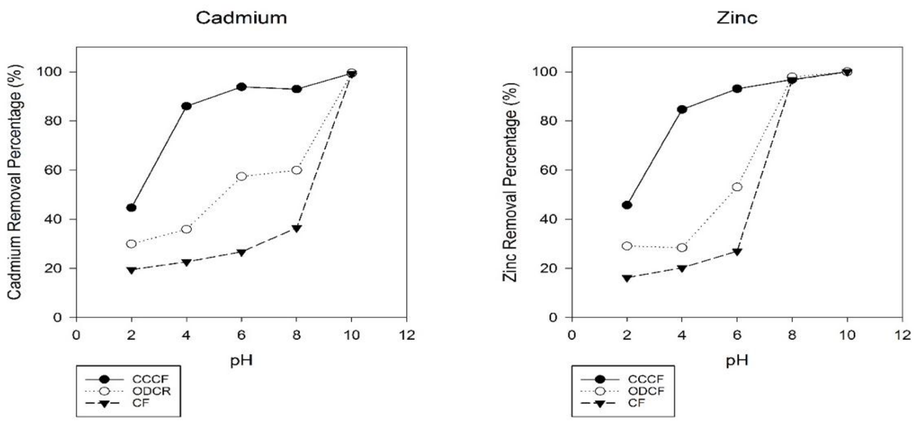

Figure 6. The effect of pH on the removal rate of each fiber.

In order study the adsorption kinetics, the Freundlich or Langmuir adsorption isotherm was usedto the present systems,. Here, the adsorption kinectic equation was fitted at different concentrations of Cd (II) or Zn (II) at 10, 20, 30, 40 and 50 ppm at pH = 6 for 2 hours.Table 1 lists the examination results of both kineties. The Langmuir isotherm of CCCF was suitable than the Freundlich isothermdue to the correlation coefficient of Langmuir (r^2 = 0.973 and r^2 = 0.937 corresponding to Cd (II) and Zn (II), respectively). As a result, the adsorption ability of CCCF was mainly obeyed to saturation mechanisum to chitosan layer on the surface. Also as seen in Table 2 for the results of sorption kinetics [12] the fitting with Freundlich kinetics was higher than that of Langmuir one, indicating that the adsorption mechanism of CF and ODCF hadthe high correlation coefficient(r^2 = 0.993, 0.997, 0.998 for CF, ODCF and CCCF, respectively).

*Table 1.*Results of analyses of adsorption isotherm for CF, ODCF and CCCF on Cd (II) and Zn (II).

Material	Cd				Zn			
	Langmuir		Freundlich		Langmuir		Freundlich	
	r^2	q_{max}	r^2	n	r^2	q_{max}	r^2	n
CF	0.810	2.564	0.844	1.233	0.601	1.678	0.720	1.361
ODCF	0.728	2.994	0.811	1.754	0.779	2.732	0.872	1.788
CCCF	0.973	8.929	0.960	1.572	0.937	8.333	0.904	1.488

Table 2. Results of adsorption kinetics for CF, ODCF and CCCF.

Material	Cadmium				Zinc			
	Pseudo first-order model		Pseudo second-order model		Pseudo first-order model		Pseudo second-order model	
	k (min^{-1})	r^2	k (g/mg.min)	r^2	k (min^{-1})	r^2	k (g/mg.min)	r^2
CF	0.018	0.893	0.05	0.993	0.037	0.722	0.0002	0.131
ODCF	0.014	0.995	0.025	0.997	0.023	0.985	0.026	0.999
CCCF	2.328	0.953	0.041	0.998	0.051	0.721	0.014	0.986

It was apparent that the pseudo second-order model was considered , since the both samples of ODCF and CCCF were compatible with the pseudo second-order model (r^2 = 0.999 for ODCF, and r^2 = 0, 986 for CCCF). But, thecorreletion coefficient of the CF was significantly lower (r^2 = 0.131), meaning different kinetics with other two systems. As a result, the adsorption mechanism for Cd (II) and Zn (II) was dependent of the adsorption capacity of the fiber adsorbers.

4. CONCLUSION

The present work described fabrication of chitosan coating cellulose fiber and application to heavy metal adsorbents. The results were compared in CF, ODCF and CCCF. The efficient removal of Cd(II) and Zn(II) was observed in the CCCF, when chitosan was coated on the fiber. It was followed that the adsorption had saturation behavior according to Langmuir model, meaning that chitosan layer enhanced effectively on the removal of the heavy metal ion.

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